

Addressing PFAS Contamination

Treatment considerations for complex applications

WATER TECHNOLOGIES

Contents

Executive summary

Per-and polyfluoroalkyl substances (PFAS) have become one of the biggest concerns in drinking water quality. This large group of man-made chemicals has been manufactured and used since the 1940s and can be found in many different commercial and industrial products. PFAS are concerning because they are highly resistant to biodegradation—over time, PFAS compounds persist in the environment and accumulate in the human body. Research has linked some PFAS to potential health impacts. The U.S. Environmental Protection Agency (EPA) has classified certain types of PFAS as likely human carcinogens.

This white paper provides an overview of PFAS, highlights the issues and emerging risks of PFAS substances and examines the considerations for treating PFAS. This issue is quickly becoming increasingly complex and uniquely different from site-to-site. Despite these challenges, there are key steps that operators can take. This white paper summarizes a best approach for characterizing site conditions, selecting technologies, and designing treatment solutions tailored to the site-specific requirements of each project.

PFAS regulations are rapidly changing. The new Biden administration has indicated that regulatory actions on PFAS will be a key priority of the EPA. EPA actions under the new leadership include re-proposing the Fifth Unregulated Contaminant Monitoring Rule (UCMR 5) to collect new data on PFAS in drinking water as well as reissuing final regulatory determinations for perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) under the Safe Drinking Water Act (SDWA).

Background on PFAS Chemicals

PFAS chemicals include PFOA, PFOS, GenX (a shorter carbon chain replacement for PFOA) and many others that have been manufactured and used around the globe since the 1940s. PFAS are found in a wide range of commercial and industrial products such as nonstick cookware, food packaging, stain and water repellents, cleaning products, polishes, waxes, paints, firefighting foams, and more. There are nearly 5,000 different PFAS compounds, some of which have been more widely used and studied than others. 1 Many chemicals in this group—especially PFOA and PFOS—are concerning because they do not break down in the environment, can move through soils, contaminate drinking water sources, and accumulate in fish, wildlife, and humans. 2,3 PFOA and PFOS are also especially worrying due to evidence linking these groups to negative health effects.

PFAS molecules are composed of a chain of linked carbon and fluorine atoms. The carbon-fluorine bond—one of the strongest in chemistry—is the main reason PFAS chemicals are used to manufacture products that resist heat, stains, grease, and water. The strength of this bond explains why PFAS chemicals do not degrade in the environment, giving them the name "forever chemicals." The robust chemical structure of PFAS also makes their destruction difficult.

The two major sources of PFAS loading to the environment include:

- Industrial wastewater discharges from facilities that either produce PFAS or use PFAS chemicals to manufacture products
- Discharges from sites where aqueous film-forming foam (AFFF) was used, or is stored, such as oil refineries, airfields, firefighting training facilities, and military bases

PFAS chemicals can also enter water resources from ambient background sources (receivers of PFAS, not original sources) which include:

- Municipal wastewater treatment plant discharge
- Stormwater runoff
- Landfill leachate
- Land application of PFAS-contaminated biosolids

U.S. Food and Drug Administration. Per and Polyfluoroalkyl Substances (PFAS).

- 2 Centers for Disease Control and Prevention. Per- and Polyfluoroalkyl Substances (PFAS) Factsheet.
- 3 EPA. Basic Information on PFAS.

Because of their widespread use and persistence in the environment, most people in the U.S. have been exposed to PFAS. 4 While the risks associated with many PFAS chemicals are largely unknown, evidence exists that exposure to low levels of PFOA and PFOS can lead to adverse health effects in humans. 5 The potential health impacts of PFOA/PFOS exposure include low infant birth weight, decreased fertility, elevated cholesterol, abnormal thyroid hormone levels, liver inflammation, weakening of the immune system, and testicular and kidney cancer. 6

Mounting public awareness and concern regarding PFAS are driving regulation efforts. Under its PFAS Action Plan, the EPA in early 2020 issued preliminary determinations to regulate PFOA and PFOS in drinking water. Several states have either proposed or adopted a standard for one or multiple PFAS, resulting in a patchwork of regulations and standards across the United States. States such as California, Michigan, Minnesota, and New York have set maximum contaminant levels for certain PFAS in drinking water. (Map 1, Page 6)

Beginning in 2000, the EPA facilitated a voluntary phase-out on the manufacturing of PFOA and PFOS that involved eight major chemical manufacturers. However, PFOA and PFOS are still produced internationally and, following the phaseout, could be imported into the United States in consumer goods such as carpet, leather and apparel, textiles, paper and packaging, coatings, rubber, and plastics. 7 The EPA in June 2020 issued a final rule giving the agency the authority to review an expansive list of products containing PFAS before they could be manufactured, sold, or imported to the U.S. 8 In November 2020, the EPA announced a new interim strategy to address PFAS loading to the environment through EPA-issued wastewater discharge permits under the National Pollutant Discharge Elimination Systems (NPDES).

Research on PFAS compounds and the impacts of PFAS contamination in the environment are extensive and ongoing. EPA researchers are developing analytical chemistry methods to detect and quantify PFAS and are gathering and assessing data on chemical toxicity and environmental exposures for PFAS of highest concern. 9 The Water Research Foundation (WRF) has conducted several investigations on PFAS. Current areas of WRF research include management, analysis, removal, fate and transport of PFAS in water.

Estimates that characterize the extent of PFAS drinking water source contamination continue to change and increase. In 2020, laboratory tests commissioned by Environmental Working Group (EWG) found PFAS in the drinking water of dozens of U.S. cities, including major metropolitan areas. These results combined with academic research that found PFAS widespread in rainwater—led EWG scientists to believe that PFAS is likely detectable in all major water supplies in the U.S., almost certainly in all that use surface water. 10

10 Environmental Working Group. EWG News Roundup (1/24): EWG Finds PFAS in Major Cities' Water, Federal Clean Energy Policies Lag Behind and More. January 2020. 2008 2012 12:30 to the Second League of Terminal Second Leagu

⁴ EPA. Research on Per- and Polyfluoroalkyl Substances (PFAS).
5 Water Quality Association PFAS

Water Quality Association. PFAS.

⁶ Water Quality Association. PFAS.
7 EPA. Basic Information on PFAS.

⁷ EPA. Basic Information on PFAS.
8 EPA. EPA Takes Action to Ston Us 8 EPA. EPA Takes Action to Stop Use of Certain PFAS in Products and Protect American Consumers. June 22, 2020.

⁹ EPA. Research on Per- and Polyfluoroalkyl Substances (PFAS).

Short-chain PFAS and GenX

Following the industry phase-out of long-chain PFOA and PFOS, different types of short-chain PFAS molecules including GenX were developed and are now used extensively as replacements. Although short-chain PFAS are assumed to have a lower bioaccumulation potential, they have other properties of concern and are already widely distributed in the environment. 11

New studies published in the beginning of 2020 by the U.S. Food and Drug Administration (FDA) highlighted the growing concern around short-chain PFAS. The research focused on a certain kind of short-chain PFAS containing fluorotelomer alcohol (6:2 FTOH), which can be found in food contact substances. The FDA conducted a scientific review and analysis of data from rodent studies and concluded that 6:2 FTOH demonstrated biopersistence, which refers to the tendency of a substance to remain inside a biological organism instead of being expelled or broken down. This differs from bioaccumulation, which implies the gradual, net accumulation of substances. While the findings were based on rodent testing, the data points to the potential that 6:2 FTOH may also persist in humans following dietary exposure. After the FDA findings were released, three manufacturers agreed to a three-year phase-out of their sales of compounds containing 6:2 FTOH for use as food contact substances in the U.S. marketplace, starting in 2021. 13

From a treatment perspective, shorter chain PFAS including GenX can be more challenging to manage and remove from waters. The presence of these compounds can drive the selection of technologies for PFAS remediation and increase the complexity of treating PFAS in water and wastewater.

Managing Regulatory Uncertainty

The regulatory landscape surrounding PFAS is complex and quickly evolving. As projects are planned, it is important to stay current and track all existing and proposed federal, state, and even local PFAS regulations up to the final flowsheet design. Operators need to be acutely aware of the differences between statutory PFAS regulations and PFAS guidelines (the latter of which are non-regulatory but may become statutory in the future). Balancing current mandates with future requirements will play a critical role in the final selection of treatment technologies including the project implementation plan. Operators should also be cognizant of situations where regulations may not align (for example, cases where projects cross state lines with differing requirements or the presence/ absence of a federal limit).

Map 1: States with standards and drinking water guidelines for PFAS in the United States as of 201913

12 U.S. Food and Drug Administration. FDA Announces the Voluntary Phase-Out by Industry of Certain PFAS Used in Food Packaging. July 2020.

13 PFAS Explained: The Growing Crisis Of 'Forever Chemicals' 6

¹¹ Environmental Sciences Europe. Short-chain perfluoroalkyl acids: environmental concerns and a regulatory strategy under REACH. February 2018.

Addressing PFAS in complex streams

Industrial discharges carrying PFAS concentrations can originate from PFAS producers as well as from plants that use PFAS in their manufacturing processes. A wide range of manufacturing sectors make products using PFAS materials. These include microelectronics, electroplating, plastics, carpeting, textile, and several more.

Treating industrial PFAS wastewater and capturing these chemicals at the source is one of the most effective ways to reduce PFAS loading to the environment. PFAS remediation strategies at industrial sites can also include treating contaminated groundwater.

The building blocks of a solution

The treatment categories—and respective technologies within each—that are used to treat PFAS wastewater and groundwater at industrial sites are listed in Table 1.

According to the EPA, the volatility, solubility, environmental mobility, and persistence of PFAS compounds make determining the appropriate method for ultimate disposal of PFAS wastes a complex issue. 14 As of the writing of this white paper, the current state of the practice with PFAS destruction is based on incineration. However, the question surrounding incineration is whether complete destruction of PFAS material is achieved.

Technical investigations are underway to answer this question and determine the necessary temperature and time requirements needed for full destruction. At the same time, novel destruction approaches such as plasma, supercritical water oxidation, and electrochemical oxidation, which could potentially be done on-site, are being looked at as possible alternatives.

In December 2020, the EPA released new interim guidance on destroying and disposing of certain PFAS and PFAScontaining materials for public comment. The new interim guidance summarizes the current state of the science on techniques and treatments that may be used to destroy or dispose of PFAS and PFAS-containing materials from nonconsumer products, including aqueous film-forming foam used in firefighting. The EPA's guidance generally covers thermal treatment, landfill and underground injection technologies that may be effective in the destruction or disposal of PFAS and PFAS-containing materials. 15

Table 1: PFAS Treatment Catergories and Technologies. The optimum flowsheet of combinded technologies at each site will depend on a range of factors.

14 EPA. Per- and Polyfluoroalkyl Substances (PFAS): Incineration to Manage PFAS Waste Streams. July 2019.

- 15 15 EPA. EPA Releases Interim Guidance on Destroying and Disposing of Certain PFAS and PFAS-Containing Materials.
- December 2020.

PFAS contamination varies from site-to-site

PFAS challenges are unique from site to site, owing to the sheer diversity of different PFAS compounds and cocontaminants that can be present. For this reason, no two treatment mitigation solutions are the same—the most effective flowsheet can differ significantly between projects.

PFAS concentrations can be dominated by long-chain species at one site and short-chain at another, while other sites may contain a mixture of the two—including many kinds of each. The feed stream, type of PFAS material, and wastewater concentration of PFAS chemicals can also fluctuate significantly. A plant that generates PFAS from its operation can generate wastewater with much higher PFAS levels compared to a facility that utilizes PFAS-containing material in its operations. These disparities impact the optimal selection of treatment technologies, both from a technical and economic standpoint.

Addressing the site-to-site complexity of PFAS requires a comprehensive analytical investigation to adequately characterize the distinct PFAS species, coexisting contaminants and other conditions that will affect the performance of treatment technologies.

The merits of a holistic approach

A holistic approach is best suited for designing treatment solutions that consider the full range of technical, economic, and regulatory drivers at each site. A treatment flowsheet developed from a holistic standpoint regards the unit operations as a complete system—technically and economically optimized as a full package, not as individual parts.

This methodology is needed for balancing the trade-offs of different treatment processes to assemble the ideal combination of technologies to treat PFAS, where the choice in one option will influence the performance or the selection of another downstream. For example:

- The technology used for the separation unit can have a significant impact on the capture unit efficiency. Case in point: using RO in the separation unit to produce a smaller volume and more concentrated PFAS stream may increase the efficiency of GAC, IX, or novel adsorbent technologies. However, if too much co-contaminant is concentrated by RO, then IX removal effectiveness is compromised.
- The performance of certain technologies that are used to treat PFAS can be better in terms of removal efficiency, total treatment capacity and final water quality than other technologies depending on whether competing organics, inorganic dissolved solids, or high levels of salt are present.
- Although GAC is kinetically slower, less efficient, and requires more media to capture PFAS, it is still very robust and therefore best suited to many applications in which multiple treatment goals are present. With feedwater containing fewer co-contaminants (such as well water), ion exchange resin is generally preferable to GAC. This is because IX possesses both faster kinetics and larger capacity, resulting in a significantly smaller investment in the associated support equipment such as tanks and pipes, valves, meters and control systems, weight bearing floor space, and ceiling (height) clearance. Additionally, IX results in less media to dispose of per unit volume of water treated, as well as less associated hauling, labor, disposal and incineration cost. The decision to use IX must be influenced by its increased sensitivity to suspended, colloidal, ionic and organic co-contaminants.
- Finally, the choice in technologies and treatment process should be reviewed against the options that are available for disposal and/or destruction. As regulatory requirements increase, the cost of disposal and destruction can be a significant cost to the economics of operating a PFAS treatment system. To best manage future uncertainty surrounding disposal and/or destruction requirements, good planning should include multiple options for final disposition of the captured PFAS.

Checklist of Considerations

As solution providers begin to evaluate each unique site through a holistic lens, the following "checklist" should be considered when selecting the most appropriate mix of treatment technologies:

PFAS constituents to be treated. By analyzing a representative stream sample, the various PFAS constituents present at each site can be identified, informing the best treatment strategy. Each PFAS should be evaluated in terms of chain length, concentration, functional groups, and charge characteristics in addition to compound diversity, feed stream variability, and potential origin or source. Understanding the specific PFAS characteristics will guide the evaluation and selection of technologies to be applied in the final treatment flowsheet.

Competing contaminants. The complexity associated with managing the competing contaminants that may be present in waste streams can be equally as challenging as treating the PFAS materials themselves. Industrial wastewater can include high concentrations of suspended solids, organics, inorganic dissolved solids, and other contaminants that can interfere with treatment equipment and processes. For example, industrial wastewater organics act as a foulant on highpressure membranes and GAC. Moreover, various anionic species can interfere with the capacity of IX technologies (therefore, the decision to use IX will depend on salt levels). Fortunately, the science on the effect of co-contaminants is evolved and well understood. This knowledge should be factored into the application of various technology unit operations for treating PFAS.

Lifecycle costs. In treating PFAS, several different but essential elements will play a role in shaping costs over the life of the project. For example, operating costs vary significantly between technologies, which are selected based on the type of PFAS species, the specific competing contaminants that are present, and the long-term goals of the project. The final flowsheet design will determine the capital costs of the project (equipment and plant footprint). Other key factors affecting lifecycle costs include the level of treatment to be achieved (driving the technology selection), the method for managing captured PFAS (disposal or destruction), as well as the costs for replacing spent materials. Creating a techno-economic model of the proposed solutions is essential for estimating system lifecycle costs and determining the key cost drivers that should influence the final treatment selection.

Site constraints (disposal and footprint). The site constraints must be evaluated in light of expected disposal requirements. With disposal/destruction, the logistics and costs of removing and transporting media off-site for final disposition should be investigated early in the project, as increasing regulatory and environmental concerns could result in changes. In terms of footprint, the existing site infrastructure and layout—and the availability of physical space for additional treatment equipment close to the stream to be treated–should be planned for within the project.

Technology limitations. The limitations of each technology option should be carefully weighed during the selection process. For instance, the removal efficiency of each treatment technology varies depending on the class, species, and chain length of each PFAS compound. It is also important to evaluate the track record of each technology for treating certain classes and species of PFAS, both at pilot and full scale. More factors include the type of waste streams that are produced from each treatment process and the requirements to manage them (disposal, regeneration, or destruction) as well as the anticipated media requirements of each technology (media life, media volume, early breakthrough of certain species). Technology limitations should also be viewed in terms of competing organic and inorganic species.

Flexibility and reliability of solutions. Many of today's commercially available water treatment technologies are supplied in modular formats that can be easily modified (such as "dual technology" media vessels), thus providing operators with the flexibility to adapt to changing conditions or regulations. Membrane elements available with the same relative dimensions can be chosen based on the rejection, flux, and pressure features. Both adsorption/capture media and separating membranes can be replaced with new and alternative technology to meet the needs of future PFAS treatment challenges. The optimum solution will offer an investment in treatment infrastructure for long-term reliability, robustness, and ease of operation.

Future proofing. The benefit of an adaptable solution also applies to the ability for plants to future-proof their sites against emerging risks, feed stream modifications, or new requirements down the road. Developing the most optimized, future-proof strategy begins with a keen understanding of the main drivers at each site that need to be accounted for. These can include a shifting regulatory landscape, anticipated changes in feed stream chemistries, or other emerging contaminants that may require removal. Further drivers include increasing public awareness and concern, an ever-expanding list of PFAS compounds, as well as improving analytics and the ability to detect contaminants at lower and lower levels, driving regulatory limits.

The components of an optimal solution

Putting a holistic framework in motion with the goal to engineer a tailored, site-specific solution entails a rigorous process of on-site analysis, testing, modeling, performance monitoring, and optimization. When implementing such a procedure, the evaluation should embrace a "technology agnostic" approach where each potential solution is given objective consideration, free of preference to any manufacturer or specific technology. The components of this methodology are listed and described below.

Analytical characterization. Each site investigation should begin with the analytical work to test feedwater and characterize the site-specific PFAS materials, residuals and competing contaminants that are present.

Lab testing. Once the contaminant profiles are known, bench testing or rapid small-scale column testing (RSSCT) allows solutions engineers to evaluate the performance and removal efficiencies of various technologies and configurations. This can include testing different materials—such as IX, GAC or novel adsorbents—to see how they perform under a range of scenarios. The evaluations can be used to assess the carbon and resin(s) breakthrough characteristics of various species, such as short-chain or long-chain PFAS compounds. If the testing reveals the tendency of a particular PFAS compound to break through early, solution engineers will know that a polishing step downstream may need to be specified.

Pilot testing. The last step involves pilot testing to evaluate multiple flowsheets on-site in real-world conditions for several weeks or months to determine the optimal combination of treatment technologies. For example, a pilot test would compare different configurations of a separation step such as RO—followed downstream by GAC, IX, and a novel adsorbent. Pilot tests help quantify technical issues that were not determined in lab tests, and can be used for performance monitoring, verifying regulatory requirements, and creating economic models of each alternative.

The benefits of a mobile trailer. Pilot tests—even smaller ones—can be expensive propositions if a structure needs to be built complete with equipment, components, pipes, instrumentation, and electrical supply. However, operators can minimize these costs by employing mobile equipment to test multiple configurations on-site to determine the best flowsheet for each application. A mobile trailer is driven to the job location to treat and test site water, greatly simplifying the logistics of the pilot test.

Chart 1: This graphic illustrates a variety of options for technology selection and arrangement commonly used in the treatment of PFAS.

Mobile solutions provide the flexibility to optimize flowsheets to each site-specific application in a cost-effective manner, providing real-world operating data to inform the technology selection and design of large-scale permanent installations.

Conclusion

Removal and disposal/destruction of PFAS is a fast-evolving issue in water treatment that presents complex treatment challenges. Mounting public awareness and concern about the potential health impacts of PFAS are pushing the EPA and state agencies to establish PFAS limits, driving the need for advanced treatment technologies and expertise in designing tailored remediation solutions.

With analytical capabilities improving and driving lower detection limits, treatment solutions should be designed with flexibility for future modifications and carefully evaluated in the context of allowing a phased approach. Additional technologies can be added as requirements demand them. This enables operators to cost-effectively adapt to the eventuality of lower PFAS limits and additional PFAS compounds to remove.

It is our intention that the recommendations included in this white paper will provide water and wastewater treatment plant engineers and operators with background, knowledge, and a logical path forward for overcoming the complexity, challenges, and evolving requirements of PFAS treatment.

The difficulty in treating PFAS stems from the evolution of PFAS chemistry, the prevalence of harder-to-treat shorter chain PFAS and GenX, as well as the presence of competing contaminants. As discussed in this white paper, PFAS treatment at sites demands a holistic approach involving characterization, analytical work, lab testing, pilot testing, techno-economic modeling, and flowsheet optimization to engineer the most effective solution.

Case Studies in Treatment

CASE STUDY #1

Applying specialty anion exchange resin to achieve broad PFAS removal

A Veolia customer faced the need to treat PFAS concentrations in their process water—a challenging blend of PFAS materials originating from their incoming source water as well as material aids needed in their process. The PFAS constituents were initially believed to be a combination of PFCAs (perfluoro carboxylic acids) and PFSAs (perfluoro sulfonic acids), but upon testing, Veolia confirmed the correct PFAS compounds to include a mix of PFOA (perfluorooctanoic acid), PFOS (perfluorooctane sulfonic acid), PFHpA (Perfluoroheptanoic acid), and PFNA (Pefluorononanoic acid). Additionally, new PFAS compounds were identified, such as PFPA (Perfluoro-2-propoxypropanoic acid), along with interfering constituents like alcohols and hydrocarbons.

Veolia engineers modeled removal and concentration technologies that included RO, carbon adsorption, and specialty anion exchange resin. After working closely with the client to evaluate the trade-offs of each option, specialty anion exchange resin was identified as the optimal technology for broad PFAS removal. The solution included a two-pass container system with anion exchange resin loaded into a lead lag configuration. Lead lag typically adds 30% to 50% to the capacity of a resin system compared to single pass and is generally preferred for long-term commitments. PFAS-out specifications were met immediately and after several months of successful run time, the system continues to perform to expectations, with PFAS reduced to a level below 0.01 ug/L.

CASE STUDY #2

A combined technology approach recovers PFASfree water for boiler feedwater reuse, enabling over \$1,000,000 in annual savings

A customer engaged Veolia to design a solution for treating a mix of PFAS materials and other components in their process water. The main challenge was to reduce the volume of PFAS-contaminated water that needed to be treated for safe disposal. Previously, the customer had been removing the waste from their site for treatment with incineration and other techniques. The customer's objective was to achieve 80% process water recovery with non-detectable PFAS levels, allowing reuse as a boiler feedwater.

On-site testing revealed more than four significant PFAS compounds resulting from feedwater intake contamination and from the addition of PFAS materials by the customer as a process aid. The specific PFAS constituents identified were PFOS (perfluorooctane sulfonic acid), PFBA (perfluorobutanoic acid), PFHxA (Perfluorohexanoic acid), and PMPA (known variously as Perfluoro methoxy propanoic acid or Perfluoro-2-methoxypropanoic acid), including several potentially interfering fluorinated compounds, some of which were not PFAS.

The solution approach would need to achieve 1) suspended solids removal, 2) concentration of PFAS into a 20% waste stream of original water volume, 3) removal of residual organics from membrane permeate, and 4) polishing of recovered 80% purified water for use as boiler feedwater. Veolia engineers evaluated the potential to use RO, carbon adsorption, and specialty anion exchange resin. To meet the customer's goal, a combined approach using all three technologies was needed.

The final treatment flowsheet includes filtration, first membrane pass, second membrane pass, carbon adsorption, and IX polishing. Following a successful pilot test, Veolia installed a full-scale mobile system. Each of the two membrane passes reduces PFAS concentration in the permeate by at least three logs of reduction, ensuring the product water is below the detection limit. PFAS-out and boiler feedwater specifications were met within the first week. By converting 80% of process water to PFAS-free boiler feedwater, the water footprint of the plant was reduced by over 80%. And, by substantially reducing the volume of treated water, the customer saves over \$1,000,000 per year in operating costs.

Further details on these two case studies can be found in the Veolia-authored technical paper, *PFAS removal in the United States.*

The table below offers a view of the advantages and disadvantages of several removal technologies:

Resourcing the world

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